

Flow Injection Extraction - Spectrophotometric Determination of Bismuth with Di-(hydrogenated tallow alkyl) dimethylammonium Chloride

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Bismuth(III) (0-25 $\mu\text{g/ml}$) is determined spectrophotometrically at 513 nm after extraction into dichloromethane of the ion associate di-(hydrogenated tallow alkyl) dimethylammonium tetraiodobismuthate. The reagent stream is distilled water, merged with 1.0 M sulfuric acid, 5% potassium iodide and 5% (w/v) ascorbic acid solution. The reagent stream is 0.2% (w/v) di-(hydrogenated tallow alkyl) dimethylammonium chloride solution. The injection rate is 15 h^{-1} . The calibration graph is linear up to 25 $\mu\text{g/ml}$. The detection limit is 0.35 $\mu\text{g/ml}$ Bi. The system is applied on water samples and copper-based alloys.

Key Words: Extraction, Flow-Injection, Bismuth, Di-(hydrogenated tallow alkyl) dimethylammonium chloride.

Introduction

Although bismuth was not known as a metal, it was used as a beauty treatment during antiquity. For nearly 150 years, low doses of Bi compounds have been excellent remedies against gastric disorders, especially for colitis, diarrhea and peptic ulcers. They were and still are used for burn bandage dressings, antiseptic powders, salves or ointments and in the treatment of venereal diseases¹.

However, bismuth-based medication has advanced greatly and its newly discovered properties surpass those of so-called "modern molecules". It is the only known active ingredient eradicating *Helicobacter* (formerly identified as *Campylobacter*) *Pyloridis*, a bacteria inflicting ulcers¹.

Bismuth determination based on the yellow-color formation of tetraiodobismuthate is very well known². Extraction of bismuth before determination using different ion-pairs, such as tetraphenylphosphonium³, tetraphenylarsonium⁴, tetrabutylammonium⁵, benzyldimethylphenylammonium⁶, and 1-naphthylmethyltriphenylphosphonium⁷, is also in use. Tetradecyldimethylbenzylammonium⁸, hexadecyltributylammonium⁹ and tetramethylenebis(triphenyl)phosphonium¹⁰ have also been reported.

The extraction of bismuth is additionally done using iodide and amides in the presence of surfactants¹¹, Cyanex 301¹², tetramethylammonium¹³ and benzyltributylammonium cations², but they are subjected to

interference and are not suitable for steel alloy analysis. Relatively speaking, very little work has been done on the determination of bismuth²⁻¹³ and many of the processes require at least 10 min to be done.

This paper reports the on line determination of bismuth after extraction of its tetraiodobismuthate with di-(hydrogenatedtallowalkyl)dimethylammonium chloride based on a previous work for the determination of Bi using a batched solvent extraction method². The method reported here is rapid, precise and has been applied to determine the presence of bismuth in copper-based alloys and natural water samples.

Experimental

Absorbances were measured at 513nm with a Bausch & Lomb spectrometer fitted with special optical glass cell (Helma), of 30 μ l volume and 10 mm path length.

Solutions were pumped using a fixed speed proportioning peristaltic pump fitted with acid flex pump tubing for organic phases and tygon tubing for aqueous phases. Samples were injected using a Rheodyne 6-way valve fitted with a bypass coil. Flow lines were PTFE tubing (0.8-1.0 mm id).

Reagents and Solutions

Di-(hydrogenatedtallowalkyl)dimethylammonium chloride solution, 0.20% (w/w), was prepared by dissolving 0.20 g of the reagent (Nobel Chemicals, Sweden) in water and diluting to 100 ml of distilled water. A 5% (w/v) Potassium iodide-5% (w/v) ascorbic acid solution was prepared by dissolving 5.0 g of potassium iodide (AnalaR, BDH) and 5.0 g of ascorbic acid (AnalaR, BDH) in distilled water and diluting to 100ml.

Bismuth(III) solution (1000 ug/ml) was prepared by dissolving 2.321 g of bismuth nitrate penta hydrate (AnalaR, BDH) in 250 ml of 1M nitric acid and diluting to 1L with water. Other diluted solutions were prepared as required.

All other reagents were of analytical grade and doubly distilled water was used throughout.

General Procedure

Samples and procedures were examined using the flow system and conditions shown in Figure 1.

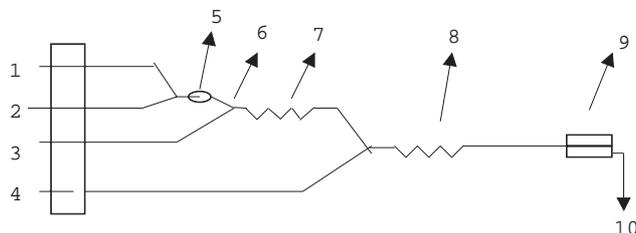


Figure 1. Flow -Injection system.

1- 1.0 M H₂SO₄, 0.76 ml/min. 2- 5.0% (w/v) KI- 5% (w/v) Ascorbic acid solution, 0.78 ml/min. 3- 0.2% (w/v) Di-(hydrogenatedtallowalkyl)dimethylammonium chloride, 0.8 ml/min. 4- Dichloromethane, 0.76 ml/min. 5- Injector (6-channel Rheodyne valve). 6- Mixing point. 7- Reaction coil. 8- Extraction coil. 9- Spectrophotometer. 10- Waste.

Procedure for copper alloys

An accurately weighed sample of Bi (500 - 1000 μg) was dissolved in 5.0 ml of concentrated HCl in a 250 ml conical flask. This solution is then oxidized with 2 ml of concentrated HNO_3 and warmed until complete dissolution. The solution is then cooled and if any residue remains it is filtered through Whatman No. 1 filter paper into a 100 ml volumetric flask. The peak heights (maximum absorbance) were measured using the conditions given in Figure 1.

The calibration curve, (0.0 - 350) $\mu\text{g}/\text{ml}$ Bi, was prepared using high purity alloys and aliquots of Bi(III) solution and proceeding as in the procedure for copper alloys.

The main experimental variables, such as effect of reagent concentration, effect of reaction coil and flow rate, were investigated using a fixed sample concentration of 15 $\mu\text{g}/\text{ml}$ and a fixed injection volume of 250 μl .

Effect of reagent concentration

The concentration of the reagent varied from 0.0 to 5% (w/v). It was found that the optimum concentration of di-(hydrogenatedtallowalkyl)dimethylammonium chloride is 0.20% (w/v). Increasing the concentration has no effect up to 5% (w/v). Higher concentrations were not easy to prepare because of the low stability of the reagent in water.

The effect of H_2SO_4 concentration (0.1-2.0 M) was also investigated. It has a fixed effect up to 0.50 M. A 1.0 M solution was used.

The potassium iodide-ascorbic acid concentrations 0.1 - 10% (w/v) was investigated. The peak height was fixed at 3% (w/v). A 5% (w/v) was used. When the concentration of ascorbic acid-potassium iodide exceeds 10.0% (w/v) some deviations from linearity were noticed, which could be due to impurities in the reagents.

The sample volume was increased from 0.0 to 1000 μl . It was found that up to 400 μl the absorbance increase with concentration is nearly linear, which could be due to peaks broadening. A 250 μl volume was chosen.

Different solvents were investigated using fixed concentrations and volumes of bismuth, 15 $\mu\text{g}/\text{ml}$ and 250 μl , respectively. Based on previous investigations, dichloromethane, dichloroethane and chloroform were the best extracting solvents. Dichloromethane was chosen for further investigation.

Effect of operating variables

The effect of extracting coil length was investigated under the optimum conditions of sample concentration and volume by varying the length from 0 to 500 cm. Absorbance was constant after 100 cm length; therefore a 150 cm length was chosen.

Results and Discussion

A linear calibration graph was obtained for 0.0-35.0 $\mu\text{g}/\text{ml}$ Bi with a slope of 5.55×10^{-3} and a correlation coefficient of 0.996 (Figure 2). The relative standard deviation for the determination of Bi(III) was less than 0.40% and the detection limit (3 x baseline noise) was 0.25 $\mu\text{g}/\text{ml}$. The effect of experimental variables, such as reaction coil, volume of injections and flow rates, have been studied. The reaction coil length varied

from 30 cm to 500 cm. There were no changes in absorbance; therefore a 50 cm reaction tube was used. The injection volume varied from 50 to 1000 μl . The best volume, which gave an appropriate peak height = 0.3 A was 250 μl . The flow rate was changed either by changing the speed of the peristaltic pump or by changing the tubes diameter. The best flow rates are given in Figure 1.

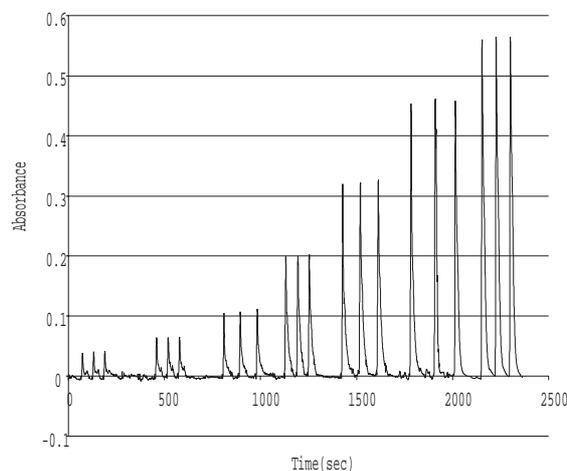


Figure 2. A flow injection output Calibration graph of Bi (5.0, 10.0, 15.0, 20.0, 25.0, 30.0, 35ppm).

The results for determination of Bi in copper-based alloys, shown in the Table were in good agreement with certified values. Investigation of the bismuth content in natural water samples (tap water) revealed no traces, indicating that the analyte was below the detection limit. However $99 \pm 1\%$ recovery was obtained for Bi-spiked samples.

Table Determination of bismuth in certified British Chemical Standards.

Copper- based alloys No.	Certified values (%w/w Bi)	*Found values (%w/w)
CURM 50.03 -4	0.051 (0.050 - 0.052)	0.051 ± 0.002
CURM 50.01 -4	0.029 (0.028 - 0.030)	0.029 ± 0.003
CURM 50.04 -4	0.100 (0.098 - 0.102)	0.099 ± 0.002
CURM 71.32 -4	0.051 (0.049 - 0.053)	0.052 ± 0.002
CURM 71.31 -4	0.027 (0.026 - 0.028)	0.027 ± 0.003

* mean \pm 95% confidence limit for 7 replicates.

Although the results in this work are nearly similar to those published in previous work² on interference study, detection limits and reaction conditions, the advantages of this FIA method over the manual-time consuming batched method in general and over the previous published work² in particular are as follows: firstly, this method is faster (15 injectionb per minute), while it took at least 5 minutes for each single run in a batched method; secondly, the reagent consumption is less, therefore, it is cheaper, thirdly this method is safer as it minimizes exposure to solvent vapors; and finally, it is more precise as the standard deviation obtained in this method is nearly half its value in² for the same reference materials.

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